



# Catalytic wet oxidation of phenol over lanthanum strontium manganite

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## ABSTRACT

The catalytic performances of lanthanum strontium manganite ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3.0}$ ), in catalytic wet oxidation (CWO) of a phenol solution under milder conditions of temperature (398–498 K) and pressure ( $P_{\text{O}_2} = 4$  bar), in a batch reactor, have been investigated. Aim of this study is the evaluation of the effect of temperature, catalyst loading, phenol concentration and stirrer speed on phenol conversion. Experimental data obtained from the different test conditions are best-fitted to evaluate the effective reaction order and apparent activation energy.

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## 1. Introduction

The contamination of aqueous streams by organic compounds is a problem of great interest today since the growing demand of quality water resources. As summarized in a recent review [1], the abatement of phenol from fluid streams has been the object of much investigation, because it and/or its derivatives are present as pollutants in wastes arising from several industrial and alimentary processes, and also because phenol is frequently taken as a model molecule for bad smelling volatile organic compound water pollutants.

There are different strategies for the remediation of water contaminated with these compounds. Adsorption on activated carbon is a widely used and effective technique for the removal of a broad range of organic compounds including phenols [2]. However, adsorption does not ultimately destroy the pollutants, therefore the active carbons have to be disposed or reactivated, which increases the costs of the method.

The conventional biological treatment is widely applied for the handling of residual wastewaters. The main disadvantage of biological treatment is the incapability of treatment for highly

polluted and toxic waste streams in industrial wastewaters. Biological treatment is neither suitable for chemical oxygen demands (COD) above  $10 \text{ g l}^{-1}$  nor for water which includes toxic compounds [3] due to biomass poisoning.

The wet oxidation (WO) process, in particular the catalytic one (CWO), is considered to be an attractive method for treatment of wastewaters with concentrations of organic loads of about  $10\text{--}100 \text{ g l}^{-1}$  [4–6]. The use of a catalyst results in a significant reduction of the temperature and pressure, an increase of the oxidation rate of refractory compounds and is therefore improving the economy of the process because the oxidation of organic pollutants can be realized under milder conditions compared to the noncatalyzed processes. As usual, a key aspect in this process is the catalyst choice, at the present time those with the best performances are noble metals-based [6,7], whose main drawback is their high cost. In the last decade, significant efforts have been done in finding new materials fulfilling important requirements as cheap cost, activity at low temperature and pressure, stability and that they are environmentally friendly. With regard to this, several groups investigated on Cu-based materials. Pintar and Levec [8–10] worked on Zn–Cu–Al-based systems under 373–403 K and 5–6 bar of  $P_{\text{O}_2}$ . Cu-based catalysts have also been investigated deeply: Eftaxias et al. [11] worked with a trickle bed reactor at 433 K and  $P_{\text{O}_2} = 6$  bar employing a  $\gamma\text{-Al}_2\text{O}_3$ -supported CuO catalyst. The group of Santos tested different copper-based materials as catalysts for phenol wet oxidation [12] in a trickle bed reactor at 413 K and  $P_{\text{O}_2} = 16$  bar. The same group investigated

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also on the employment of active carbons as catalysts under the same conditions [13].

Recently, interest has been devoted to Mn-based catalysts. Hamoudi et al. investigated on ceria-supported  $\text{MnO}_2$  [14,15] obtaining interesting phenol conversion under very mild conditions namely 50 bar of  $\text{O}_2$  partial pressure at ca. 373 K. Chen et al. [16] studied the effects of Mn–Ce–O composites on phenol catalytic wet oxidation at low  $\text{O}_2$  partial pressure and temperature. The group of Stoyanova published great results [17] in phenol abatement under atmospheric pressure and almost room temperature (308 K) employing a Ni–Mn mixed oxide.

However, it must be taken into consideration that phenol may be not totally directly oxidized to  $\text{CO}_2$  by CWO, a range of organic compounds being formed as intermediates or byproducts during the mineralization process. The hydroxylation of phenol to hydroquinone and catechol is considered to be the first step followed by a further oxidation of the dihydroxybenzenes to benzoquinones [5]. It is also assumed that both dihydroxybenzenes follow the same oxidation route leading to various C-4 products such as maleic acid or C-2 products like oxalic acid and acetic acid [5]. Since some of the intermediates, in particular hydroquinone and *p*-benzoquinone, are more toxic than the original pollutant [18,19], the identification of the products at the end of the oxidation process is a key point to evaluate the reduction of ecotoxicity actually obtained with the process.

A main drawback of CWO with most impregnated transition metal oxide catalysts is their leaching, which results in solid catalyst deactivation as well as in water contamination by the metal ions. As pointed out by Pintar and Levec [6], to limit leaching, transition metal ions should be incorporated in the solid more than deposited at his surface.

Perovskite-type oxides ( $\text{ABO}_3$ ) containing transition metals such as Mn have been studied as potential combustion catalysts [20–23] ever since it was discovered that some have comparable catalytic activities to conventional  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts [24]. In particular  $\text{LaMnO}_{3+\delta}$  is one of the perovskite oxides easier to reduce therefore suitable as catalyst for oxidation reactions; its catalytic activity is strictly related to the nonstoichiometric character of the surface [25,26]. Also, the incorporation of dopant ions, commonly low valent cations such as  $\text{Sr}^{2+}$ , to the  $\text{LaMnO}_{3+\delta}$  oxides results in a promotion of the catalytic activity lanthanum strontium manganite ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ ) powders, called LSM, is an excellent combustion catalyst in gas–solid processes [20], and is commercially available being, among other applications, used to produce anodes of solid oxide fuel cells by sintering. Perovskite-like oxides recently found application as catalysts in CWO of stearic acid, interesting results were published in [27].

Aim of this work is to investigate on the activity of ( $\text{La}_{1-x}\text{Sr}_x$ ) $\text{MnO}_{3+\delta}$  as catalyst in phenol CWO, as well as on the optimization of the process parameters as temperature, catalyst load and agitation speed.

## 2. Experimental

### 2.1. Catalyst

The catalyst was a commercial (Praxair) perovskite-like ( $\text{La}_{0.8}\text{Sr}_{0.2}$ ) $\text{Mn}_{0.98}\text{O}_3$ .

X-ray powder diffraction pattern of the sample was carried out with a X-Pert Philips diffractometer using a  $\text{Co K}\alpha$  radiation.

The microscopic analysis by scanning electron microscopy (SEM) was carried out in a Jeol SM-840 instrument that allowed to obtain information about the morphology.

### 2.2. Catalytic activity tests

Catalytic activity test were conducted in a stirred batch reactor (“4563 Mini reactor”, produced by the Parr Instrument Company, IL, USA). It consists of a moveable cylindrical stainless steel 0.6 l vessel with a flat gasket seal. It is equipped with a gas inlet valve, a gas outlet valve, a liquid outlet valve and a rupture disc as a pressure relief device. Temperature and pressure can be checked by an internal fixed thermocouple and by a pressure gauge. The vessel can be heated by a cylindrical heater; inner liquid solution can be stirred by a stirring system.

The reactor was loaded with 0.5 l of phenolic solution at fixed concentration and with the catalyst in powder form. The reactor was then sealed and pressurized with oxygen through gas inlet valve to an initial pressure of 4 bar. Catalytic tests were carried out by varying temperature, phenol concentration, catalyst loading and the stirrer speed. Blank experiments (i.e. with no catalyst) at 423 and 448 K were conducted as well.

The solutions were analyzed by HPLC (Shimadzu 10 A VP system equipped with a diode array detector). The column employed was a Pinnacle II C18 with a length of 250 mm and an inner diameter of 4.6 mm. The stationary phase is C18 or ODS silica supported with a media particle diameter  $d_p$  of 5  $\mu\text{m}$ . The mobile phase employed in this work was a mixture of acetonitrile (35%) and water (65%) sent through the column with a flow rate of 0.7  $\text{ml min}^{-1}$ . The water employed in the mobile phase was deionized, micro-filtrated and furthermore acidified with 1 ml of  $\text{H}_3\text{PO}_4$  (3 M) resulting in a pH of 2.8.

## 3. Results and discussion

### 3.1. Catalyst characterization

The physical properties supplied by the manufacturer (Praxair) are:  $d_{50} = 0.9 \mu\text{m}$ , surface area =  $5.0 \text{ m}^2 \text{ g}^{-1}$ .

X-ray powder diffraction pattern of the sample, reported in Fig. 1, confirms the perovskite structure of ( $\text{La}_{0.8}\text{Sr}_{0.2}$ ) $\text{Mn}_{0.98}\text{O}_3$ .

SEM micrograph of the fresh sample, reported in Fig. 2, shows the homogeneity of the microscale crystal size of the powders.

### 3.2. Catalytic behaviour

Fig. 3 shows the trends of phenol conversion (Fig. 3a) with the temperature and reaction time, as well as the trends of the selectivities to cyclic intermediates, *o*-benzoquinone (Fig. 3b), hydroquinone (Fig. 3c) and *p*-benzoquinone (Fig. 3d). The

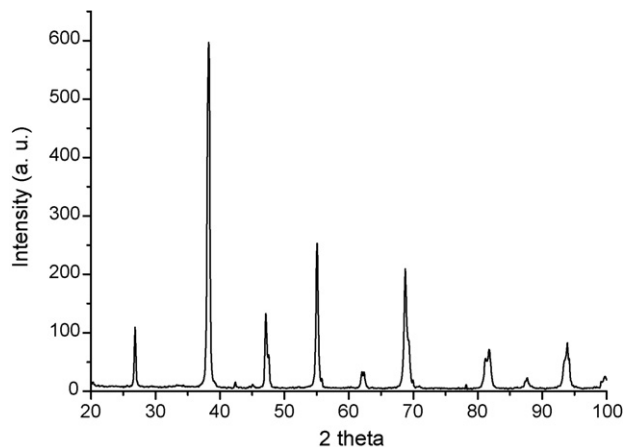


Fig. 1. X-ray powder diffraction pattern of ( $\text{La}_{0.8}\text{Sr}_{0.2}$ ) $\text{Mn}_{0.98}\text{O}_3$ .

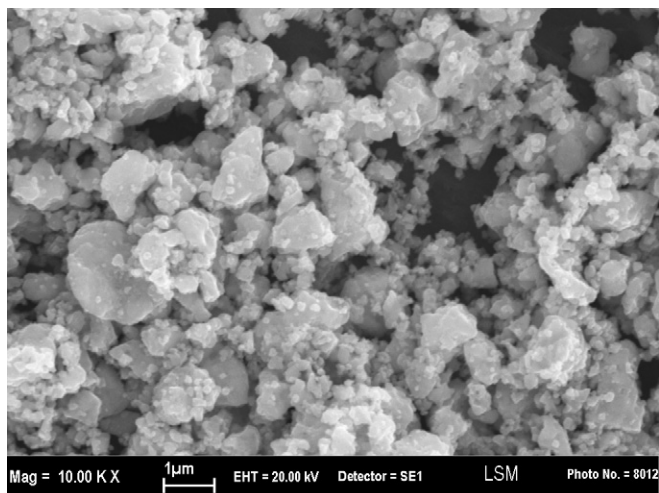


Fig. 2. SEM micrograph of a fresh sample of  $(\text{La}_{0.8}\text{Sr}_{0.2})\text{Mn}_{0.98}\text{O}_3$ .

conversion of phenol at zero time is already significant in the experiments performed at 448, 473 and 498 K since the zero time is considered the time at which the reaction temperature is reached. The reaction rate is definitely lower at 423 K compared with higher temperatures, where the effect of temperature on reaction rate is much smaller. After 5 h the conversion of phenol is 85% at 423 K, 88% at 448 K while it is almost total at higher temperature (97% at 473 K and 99% at 498 K).

The selectivity to cyclic intermediates is always very low (never exceeding 2% in total). In the first hour of treatment the main cyclic

intermediate is *o*-benzoquinone (Fig. 3b) which selectivity reaches 1.7% at 423 K, but decreases with time as well as by increasing temperature.

The selectivities to hydroquinone and *p*-benzoquinone have different trends, and some parallelism each other. At 423 K they appear after 1.5 h of reaction and the selectivities never exceed 0.1% till the end of the treatment. A raise in the temperature results in an increase of the selectivity to hydroquinone at lower time and in a decrease at higher time. The maximum of selectivity to hydroquinone reached is 0.6% at 498 K. As for *p*-benzoquinone an increase of the temperature results in an increase of the selectivity during the whole reaction time. Under these conditions the selectivity to *p*-benzoquinone does not exceed 0.6% at 498 K. The highest yields to hydroquinone and to *p*-benzoquinone, at the end of the phenol oxidation process, are respectively 0.28% and 0.58%. Final organic products in solution after 5 h are short chain organic acids, i.e. maleic, malonic, acetic and oxalic acid. The highest value of selectivity to acetic acid after 5 h is 26.5% at 423 K. At higher temperature the selectivity to acetic acid is lower, about 18% after 1 h and it decreases to 15% after 5 h.

These data show that our catalyst is very active in converting the toxic cyclic intermediates cathecol, hydroquinone and *o*- and *p*-benzoquinone to noncyclic smaller molecules and to carbon oxides. This has been confirmed by performing experiments of their oxidation in the same conditions. The appearance of small amounts of hydroquinone and *p*-benzoquinone only after 1 h of reaction at 423 K, and the increase of their selectivity with time at all temperatures suggest that the appearance of these molecules among the products is in some way indicative of catalyst deactivation.

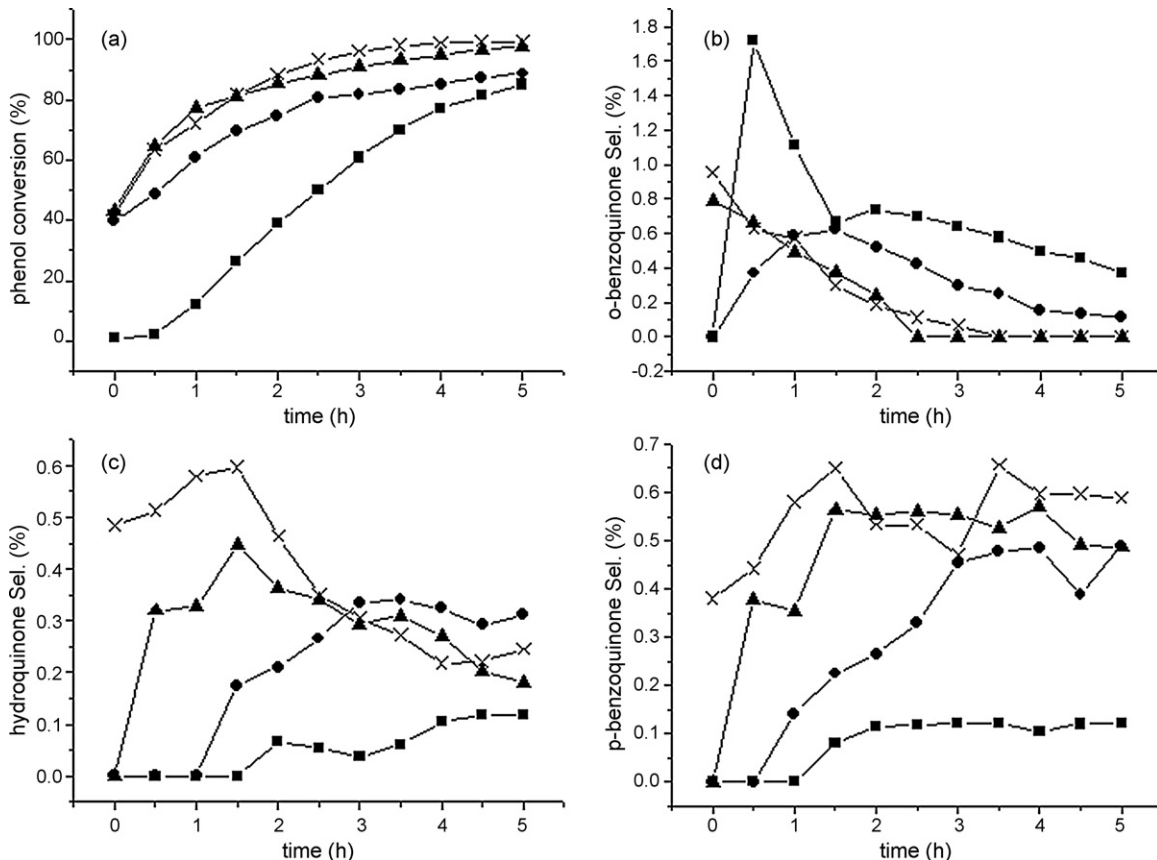


Fig. 3. (a) Phenol conversion (%) vs. time (h), (b) *o*-benzoquinone selectivity (%) vs. time (h), (c) hydroquinone selectivity (%) vs. time (h) and (d) *p*-benzoquinone selectivity (%) vs. time (h) at: ■ 423 K, ● 448 K, ▲ 473 K and × 498 K.  $C_{\text{phenol}} = 6.25 \times 10^{-4}$  M,  $W_{\text{cat}} = 2$  g  $\text{l}^{-1}$ ,  $P_{\text{O}_2} = 4$  bar, stirrer speed = 480 rpm.

### 3.3. Kinetic evaluations

The kinetic analysis of the reaction was performed by evaluating the effects of phenol concentration and catalyst loading, temperature and stirring speed. The experimental data displays (with a satisfying best-fit) a first-order-like kinetics with respect to phenol concentration, confirming some literature findings [28–30].

$$\frac{dC_{\text{phl}}}{dt} = -KC_{\text{phl}} \quad (2)$$

where  $C_{\text{phl}}$  is the concentration of phenol ( $\text{mol cm}^{-3}$ ) and  $K$  is the rate constant including all other kinetically relevant factors such as oxygen partial pressure, mass transfer phenomena (i.e. mixing) and catalyst load. Since oxygen is fed in large excess with respect to the stoichiometry, it can be considered as a constant. As expected, as temperature increases, the rate of conversion increases since also correlated phenomena increase.

### 3.4. Effect of the initial phenol concentration

Fig. 4 shows the conversion  $x$  vs. time curves, modelled with a first-order-like kinetics, at different initial phenol concentrations at 423 K. Though the time required to reach an asymptotic regime is almost constant as the initial phenol concentration increases, the imposed catalyst loading along with the fixed agitation speed do not allow a complete conversion of phenol, probably due to mass transfer limitations between gas-phase and liquid-phase oxygen and transport limitations of phenol to the catalyst surface. The conversion of phenol decreases by increasing phenol concentration. This effect can be indicative of some kind of phenol self-inhibition, i.e. of partial deactivation by phenol or transport limitations of phenol to the catalyst surface. For this reason the effect of the catalyst loading and stirrer speed have been studied.

### 3.5. Effect of the catalyst loading

At a constant initial phenol concentration the effect of the catalyst loading on phenol conversion was studied by varying the catalyst concentration at 448 K (Fig. 5). The initial rate of phenol oxidation per gram of catalyst decreased by increasing the catalyst

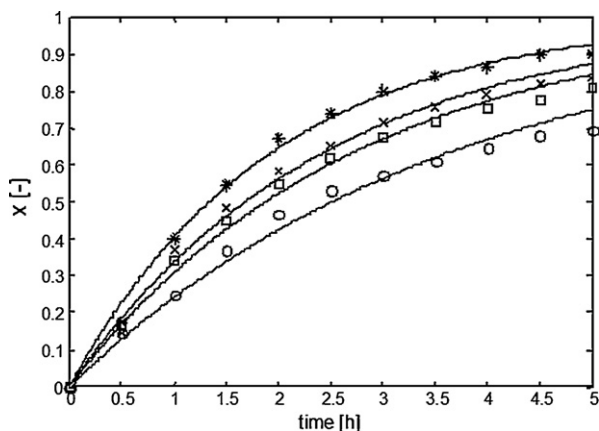


Fig. 4. Effect of different initial phenol concentrations on phenol conversion at 423 K, oxygen pressure = 4 bar, stirrer speed of 480 rpm and catalyst loading =  $2 \text{ g l}^{-1}$ . \* [PhOH] =  $3.75 \times 10^{-4} \text{ M}$ ; × [PhOH] =  $6.25 \times 10^{-4} \text{ M}$ ; □ [PhOH] =  $7.50 \times 10^{-4} \text{ M}$ ; ○ [PhOH] =  $1.25 \times 10^{-3} \text{ M}$ .

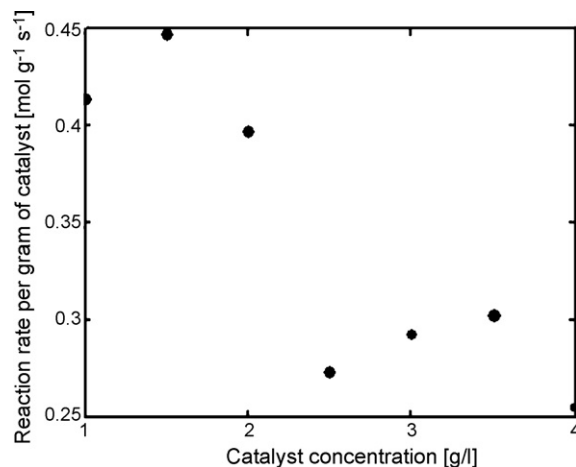


Fig. 5. Effect of catalyst concentration on reaction rate per gram of catalyst at 448 K, oxygen pressure = 4 bar, stirrer speed of 480 rpm and phenol initial concentration =  $6.25 \times 10^{-4} \text{ M}$ .

loading till  $2.5 \text{ g l}^{-1}$  and became almost independent of catalyst concentration at higher loadings.

The behaviour of phenol oxidation rate at catalyst concentrations lower than  $2.5 \text{ g l}^{-1}$  suggests transport limitations of phenol to the catalyst surface. At higher catalyst concentrations, the reaction rate per gram of catalyst seems to be less affected by catalyst loading, indicating that a kinetic control seems to prevail on transport limitations.

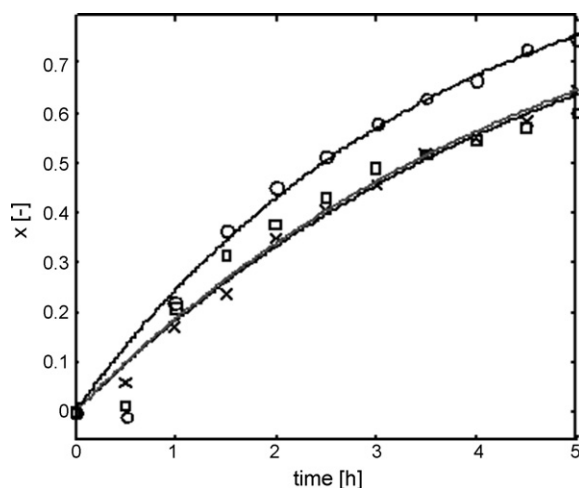
The apparent activation energies estimated from the slopes of the straight lines in Arrhenius plots and calculated by means of the least squares technique, in case of catalyst loading of  $2 \text{ g l}^{-1}$ ,  $3 \text{ g l}^{-1}$  and  $4 \text{ g l}^{-1}$ , were respectively  $32.5 \text{ kJ mol}^{-1}$ ,  $42.7 \text{ kJ mol}^{-1}$  and  $44.6 \text{ kJ mol}^{-1}$ . The values obtained indicate that catalyst loadings above  $2.5 \text{ g l}^{-1}$  introduce a change in the reaction regime, thus becoming mainly kinetic controlled even though the rather low values of the apparent activation energies reveal that diffusion limitations still have an effect on the reaction rate. Table 1 shows some of the apparent activation energy values available in literature, our data are in rough agreement with those obtained by Kochetkova et al. [28] employing an alumina supported Cu-based catalyst. The data reported in Table 1 seem to show the highest apparent activation energies for high oxygen pressure experiments. This may be an indication that oxygen diffusion is actually limiting the reaction.

### 3.6. Effect of stirring speed

In a stirred batch reactor, the mixture is stirred vigorously in order to slurry the catalyst uniformly throughout the liquid. In order to observe the effect of the stirrer speed on the phenol oxidation rate, experiments were carried out at different stirring speeds (Fig. 6). As the stirring speed increases from 0 rpm to

Table 1  
Literature data for apparent activation energy for CWO of phenol

Catalyst [Ref.]	T (K)	$P_{\text{O}_2}$ (bar)	App. $E_{\text{act}}$ ( $\text{kJ mol}^{-1}$ )
ZnO CuO $\text{Al}_2\text{O}_3$ [8]	378–403	5.6	84
Cu (chromite) Zn Al [32]	403	20	139
Pt/TiO <sub>2</sub> [33]	448	48 (air)	125
CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$ [11]	433	6	74.9
10% CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$ [34]	386–418	6–14	85.4
Cu-based/ $\gamma$ - $\text{Al}_2\text{O}_3$ [28]	392–444	4–12	53.6
(La <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub> [t.w.]	448	4	44.6



**Fig. 6.** Effect of stirrer speed on phenol conversion at 448 K, oxygen pressure = 4 bar, catalyst loading =  $1 \text{ g l}^{-1}$  and phenol initial concentration =  $6.25 \times 10^{-4} \text{ M}$ .  $\times$  speed off;  $\square$  speed 480 rpm;  $\circ$  speed 700 rpm.

480 rpm, no appreciable differences on conversion are detected; on the other side, phenol conversion increases appreciably at 700 rpm, ensuring vigorous mixing and uniformity throughout. The existence of a threshold value is suggested in which the resistance due to phenol mass transfer to the catalyst particle has overcome.

### 3.7. Intraparticle diffusion limitations, Thiele modulus, effectiveness factor

To exploit if intraparticle diffusion is the controlling mechanism for mass transfer in the catalyst particles, and Fick's law applies, it is necessary to plot the effectiveness factor  $\eta$  as a function of Thiele modulus  $\Phi$ , through (3), valid for a first order reaction in a

spherical catalyst particle:

$$\eta = \frac{1}{\Phi} \left( \frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi} \right) \quad (3)$$

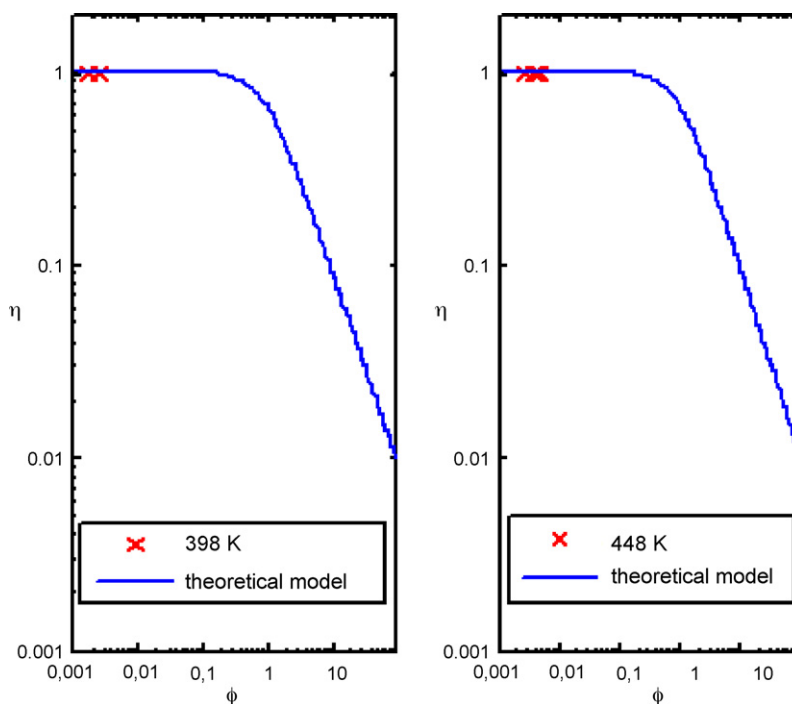
Fig. 7 shows that, at both 398 K and 448 K, the small diameter of the particles, as conceivable, “forces” the diffusion rate to be much larger than the reaction rate and lets the effectiveness factor  $\eta$  stand near unity, thus not to spring out intraparticle diffusion limitations. Therefore, the surface throughout the inside of the catalyst particle is exposed to reactant of the same concentration as that existing at the outside surface of the particle utilized, under the simplified assumptions of porous structure spherical in shape and isothermal, diffusion of the species governed by Fick's law, irreversible first-order reaction, steady state conditions.

### 3.8. Discussion on physical characterization

Since the encouraging preliminary results collected a further deep characterization of the physical properties of LSM is opportune to better understand the exact mechanism of CWO at the surface.

The catalytic activity of perovskite-like oxides in oxidation reactions is strictly related to the nonstoichiometric character of the surface, therefore a determination of parameters like oxygen storage capacity (OSC) and/or oxygen mobility is very important, the group of Duprez and coworkers intensely worked on this topic [25–27].

In order to have reliable data it is fundamental to realize in situ measurements of OSC and/or oxygen mobility taking into consideration every aspect, like the presence of water for instance, that could have an influence on this measurements. Since the complexity of this subject we preferred to discuss the catalytic activity results separately from the catalyst physical characterization which is matter of our next research project on this topic.



**Fig. 7.** Effectiveness factor vs. Thiele modulus at 398 K and 448 K.



#### 4. Conclusion

This study exploited the applicability of lanthanum strontium manganite for catalytic wet oxidation of phenol. This material appears quite interesting due to its significant activity at low oxygen pressure, with a very small formation of toxic products hydroquinone, *p*- and *o*-benzoquinone. The kinetic of the reaction exhibited first-order-like behaviour with respect to phenol concentration. The reaction rates per gram of catalyst show a dependence on catalyst loading, decreasing as the catalyst concentration increased until a threshold value is reached. These observations suggest transport limitations of phenol to the catalyst surface, as already advised by Satterfield [31], although these limitations may be overcome by increasing the catalyst loading. Besides, an increase in stirring speed increased conversion of phenol appreciably, with a thresholding behaviour.

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